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TREATMENT OF PHOSPHORUS BURNS*

(WITH A NOTE ON ACUTE PHOSPHORUS POISONING)

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Introduction: This outline is based upon information obtained from the British War Office, the British Ministry of Home Security and other official sources; experiences in the laboratories of the Imperial Chemical Industries Ltd., the Crookes Laboratories and others¹ and the writer's experiences with air raid precautionary measures in England and chemical warfare and toxicological research in general. The series of publications on air raid precautionary measures, of which this is one, aim at giving the best available information and will be revised from time to time in the light of future developments.

Types of Phosphorus

Phosphorus is probably too active to occur in the free state in nature. It is obtained on a commercial scale by treating naturally occurring compounds of phosphorus (calcium phosphate, etc.). Like sulphur, it exists in allotropic forms, and there are at least five types—red, scarlet red, violet, black and white. The two common forms are the red and white, and the contrast in their appearance and other properties is so great that a casual observer would hardly suppose that they are the same element. Since red phosphorus does not possess any of the properties with which this paper is con-

cerned—the capacity to burn and poison—the following observations refer to white phosphorus only.²

Occurrence. — In peace-time, phosphorus is used in a number of industries, pyrotechnical, alloys, etc. In war, it serves a variety of purposes. It is a very efficient material for generating smoke screens and, because of its incendiary properties, it is used in small arms incendiary bullets, in hand and rifle grenades, in artillery incendiary shells, in trench mortar bombs and in bombs dropped from aeroplanes, A marked increase of phosphorus burns may, therefore, be expected as the war progresses. Phosphorus is also employed in "tracer" bullets and, recently, has been incorporated by the Germans into the .312 Mauser machine gun bullets in sufficient quantities to cause death, and, in fact, has caused death, from acute phosphorus poisoning.

Chemical and physical properties.3 — White phosphorus, when pure, is a translucent, lustrous solid of waxy consistency, soft at ordinary temperatures and brittle when cold, and has a strong odour of matches. It is about twice as heavy as water (specific gravity = 1.8) and melts at 44.2° C. (112° F.), that is, at a temperature of very warm water. It is almost insoluble in water, soluble in oils and very soluble in carbon disulphide. Solutions of phosphorus in carbon disulphide form explosive mixtures with air at ordinary temperatures, and the finely divided phosphorus which is left on evaporation of the carbon disulphide ignites spontaneously. Phosphorus is soluble in a variety of other organic solvents, some of which are also highly Some of these solvents also dissolve rubber and thus make possible the preparation of phosphorus-rubber incendiary mixtures.

Phosphorus unites readily with oxygen in

^{*}Published by authority of Hon. I. A. Mackenzie, K.C., M.P., Minister of Pensions and National Health and Hon. R. J. Manion, M.C., M.D., Director of Civil Air Raid Precautions.

^{1.} Brit. M. J., 1941, 2: 428; ibid., 1942, 1: 433; ibid., 2: 244, 644, 767; ibid., 1943, 1: 111, 128.

^{2.} Red phosphorus does not ignite in air below 240° C. (464° F.) and, as a poison it is relatively inert.

^{3.} This description is confined to chemical and physical properties which are of clinical importance.

the air and produces phosphorus pentoxide⁴ $4 P + 5 O_2 = {}_{2}P_{2}O_{5}$.

The oxidation is accompanied by evolution of light, although the temperature is not such as is usually associated with incandescence. Phosphorus thus becomes luminous in the dark. As will be seen later, this is taken advantage of in the treatment of phosphorus burns. The luminescence is usually pale green or faint bluish in colour. In warm air (35° C.), the oxidation takes place with such energy that the element bursts into a yellow flame (hence its use in tracer bullets) and produces a dense white smoke.⁵

Burning phosphorus is easily extinguished with water, but *re-ignites on drying*. For this reason materials contaminated with phosphorus during air raids must be kept wet until the phosphorus has been removed.

The oxides of phosphorus unite with water to form acids. $P_2O_5 + 3 H_2O = {}_2H_3PO_4$ (phosphoric acid). $P_2O_3 + 3 H_2O = {}_2H_3PO_3$ (phosphorous acid), etc.

Phosphorus unites directly with metals to form phosphides. For example, when placed in solutions of copper salts, it forms nonigniting black copper phosphide. The ratio of copper to phosphorus in the compound is, however, constant under certain carefully regulated conditions only. During this reaction, various phosphorus and other acids are produced. Thus, if copper sulphate is used to stop the ignition of the phosphorus, sulphuric acid is produced, in addition to the phosphorus acids and thus adds to the acidity of the mixture.

Pathology. — When phosphorus comes into contact with skin and is allowed to burn, it produces almost immediately a greyish discoloration of the affected part. The initial pain is very severe and in severity the burns approach those produced by hydrofluoric acid and, thus are more severe than those produced by caustic soda, sulphuric acids or other acids. The phosphorus tends to imbed itself in the skin and the phosphorus acids produced tend to penetrate still deeper. Blisters are, however, rare. Phosphorus burns suppurate more than ordinary burns and heal slowly (3 to 4 weeks or more). The danger of infection is thus

correspondingly increased. The sears of the healed burns tend to be thin and atrophic.

White phosphorus is exceedingly poisonous (see later). Even the vapours are dangerous.

FIRST AID TREATMENT OF PHOSPHORUS BURNS

The treatment in the field is based upon the melting point of phosphorus and the fact that, while burning, phosphorus gives off phosphoric acid which itself causes the skin to burn. At the first aid post advantage is taken of the interaction between copper and phosphorus to form non-igniting black copper phosphide. Briefly, the instructions to first aid personnel are as follows:

(a) In the field.—Remove contaminated clothing at once (cut it off, if necessary) and flush the affected parts of the skin with warm (but not hot) water. Remove visible particles of phosphorus with a forceps while the skin is being flushed, taking care to remove every particle possible. Then apply a thick pad soaked in warm water. (The warm water, by melting the phosphorus, will remove phosphorus particles which have imbedded themselves in, and are adhering to, the skin more effectively than forceps. The water also dilutes the phosphorus acids produced and thus renders them less harmful.)

If the burns are extensive, evacuate the casualty to a hospital at once. If the burns are small, evacuate the casualty to the nearest first aid post.

(b) At the first aid post.—Flush the affected parts with a warm solution of baking soda or washing soda (made by adding two tablespoonfuls of the soda to a pint of warm water). (Thorough alkalinization of the affected area neutralizes the phosphorus acids and thus renders them harmless.) Then wash the last traces of phosphorus away with a 1% solution of copper sulphate and, with forceps, remove any dark-coloured (blackened) particles noted. Finally, wash the affected parts with water containing a little of any antiseptic solution and apply a sterile dressing.

Note: First aid personnel should be warned not to use oily or greasy dressings, since they do not possess the necessary facilities to determine whether all of the fragments of phosphorus have been removed. By dissolving the phosphorus oils and greases may assist its penetration into the deeper tissues and thus increase the depth and severity of the burn.

^{4.} In the presence of a restricted supply of air, phosphorus trioxide (P₂O₃) is formed.

^{5.} A phosphorus bomb is recognized by the smell and the dense white smoke which it produces.

MEDICAL TREATMENT OF PHOSPHORUS BURNS

The first aid treatment described aims at simplicity and speed, and very little other treatment will be necessary in the majority of cases, if the burns are small, few in number and have been produced by phosphorus in a form which can be readily attacked with water and aqueous solutions of copper sulphate.

Consideration must, however, be given to all forms of phosphorus which may be met with in war time. These include (a) phosphorus in a variety of organic solvents; (b) phosphorusoil preparations, and (c) mixtures of phosphorus and rubber. In burns produced by such preparations flushing of the affected parts with water, aqueous solutions of sodium carbonate or sodium bicarbonate and aqueous solutions of copper salts may not be very effective owing to the immiscibility of these organic solvents and oils with water. The effectiveness of such treatment will be still less in cases of highly viscous mixtures of phosphorus and rubber. Attempts have, therefore, been made to prepare inactivating agents to meet such conditions, and the preparation developed in the Imperial Chemical Industries, Ltd., appears to be the most satisfactory. It is an oily preparation and contains a copper compound which converts phosphorus into non-igniting copper phosphide. The organic solvent which it contains not only dissolves the copper compound and oils but also rubber. The whole preparation, therefore, is readily miscible with organic solvents, oils and rubber and thus allows intimate contact of the inactivating copper with phosphorus either in organic solvents or in oils or in solutions of rubber. The copper thus reacts progressively with the phosphorus in such solutions, not merely inactivating the surface by coating it with copper phosphide.

The authors of this formula have shown that when phosphorus, in solution of carbon disulphide, is applied to skin and allowed to ignite after evaporation of the disulphide, it is immediately extinguished by this oil-soluble copper preparation and the inactivation of the phosphorus begins almost at once. Since the preparation is easily emulsified with water it can bring about intimate contact of the copper with phosphorus even in highly viscous mixtures of phosphorus and rubber. Also, as the authors state, since the preparation contains its own emulsifying agent, it is completely removed from the skin by water, carrying with it any oil or rubber that may have been associated with the phosphorus, as well as the detritus from the inactivating reaction. The skin is left almost entirely clean and unstained. Its composition is as follows:

Copper oleate	25	grams
Trichlorethylene	35	""
Turkey-red oil ⁶	25	"
"Surgical spirit"		

The copper oleate is dissolved in the trichlorethylene. The Turkey-red oil is then incorporated into the mixture and the alcohol⁸ is added to the final mixture. The final solution is deep blue-green in colour and perfectly homogeneous. It is readily prepared.

I have tested this preparation with a variety of phosphorus-oil, phosphorus-rubber and phosphorus-oil-rubber compositions, prepared with suitable solvents and which ranged in viscosity from thin liquids to the highly viscous rubber "cements" and found it effective in practically all cases.

DETAILS OF TREATMENT STAGE 1

If the first aid treatment described has not as yet been carried out, the preliminary measures—rapid removal of clothing (if necessary) and flooding of the affected parts of the skin with warm water (over 112° F.)—are the same. The next procedure (Stage 2) depends upon the availability of the different inactivating agents. Thus:

STAGE 2

(a) Sodium carbonate or bicarbonate only available.—If neither the aqueous solution of copper sulphate nor the oil-soluble copper reagent is available, the affected parts should be washed with warm sodium bicarbonate or sodium carbonate solution (made by adding 2 tablespoonfuls of the dry product to a pint of The affected area should then be searched carefully in the dark for luminous particles of phosphorus, which should be re-

^{6.} Sulphonated castor oil, 70% ammonia-finished.

^{7.} Methylated spirit, unpyridinized, containing one-half ounce castor oil and 1 3/5 drachms boric acid to

^{8.} The alcohol is essential in cases of compositions containing rubber.

^{9.} Swabs must be wetted with the solution. suspected of containing phosphorus must not be dabbed with dry materials.

^{10.} Experiences with industrial accidents in the past have shown that the essential feature of all forms of treatment is the immediate flooding of the area with warm water and thorough alkalinization.

moved with a forceps. The skin should then, again, be washed with the alkaline solution and again examined for luminous particles, and the whole process should be repeated until the affected area is clean. The affected parts should then be soaked for a prolonged period in the warm alkaline solution (about one-half hour if the burns are small and one to two hours in the case of large burns). The subsequent treatment is as for chemical burns in general (see Stages 3 and 4).

(b) Alkaline powder mixture available.—The alkaline powder mixture developed in the Crookes Laboratories, if available, is superior to sodium bicarbonate or sodium carbonate solutions, because of its greater alkalinity and its emulsifying properties. By its emulsifying action, it facilitates the break-up of the phosphorus globules and thus permits their more rapid inactivation. It consists of the following:

Magnesium oxide (heavy)	10	parts
Borax	5	"
Sodium bicarbonate	85	"

After having extinguished the burning phosphorus with warm water, the powder is sprinkled on the wet surface and, if necessary, more water is added, and the powder is worked up to a medium thick paste. It is then washed or wiped off and reapplied so long as marked effervescence continues. A medium thick paste is then again applied, covered with a bandage and kept damp (about one-half hour if the burns are small and one to two hours in the case of large burns). The subsequent treatment is as for chemical burns in general (see Stages 3 and 4).

(c) Copper sulphate available.—If an aqueous solution of copper sulphate is the only copper preparation available, the affected area should be washed with it immediately after the first alkaline treatment and the removal of the luminous particles in the dark described above. A very careful search should then be made for any blackened particles of copper phosphide¹¹ which should be removed. The affected parts

should then be soaked for a prolonged period in warm sodium bicarbonate (about one-half hour if the burns are small and one to two hours in the case of large burns). If the alkaline powder is available it should be used as described instead of the prolonged soaking. The subsequent treatment is as for chemical burns in general (see Stages 3 and 4).

(d) Oil-soluble copper preparation available.

—If the oil-soluble copper reagent is available, it should be applied to the affected area immediately after the preliminary flooding of the affected parts with warm water, by swabbing, pouring or by actual immersion of the affected parts, as the circumstances require.

NOTE: If the burns are widely scattered and cannot be treated at the same time with the oil-soluble copper reagent, the untreated parts must be kept wet until they can be treated.

In general, inactivation of the phosphorus will take place in from a few seconds to one or two minutes. When the inactivation has been well established, the affected areas should be washed with tepid water and all of the contaminated material should be swabbed off. The whole area should then be thoroughly alkalinized with sodium bicarbonate paste as described above.

STAGE 3

After the skin has been finally alkalinized by any one of the methods described it may be dressed daily with a 1:1,000 acriflavin emulsion or treated with some other antiseptic, but the following points are to be noted:

- (a) Acriflavin emulsions might produce skin eruptions. Therefore, if they are used, the affected area should be examined daily and the emulsion should be discontinued immediately after any eruption is noticed.
- (b) "Sulpho" pastes and emulsions appear to be satisfactory, but they also might produce skin eruptions and should be discontinued as soon as any eruption is noted.
- (c) Tannic acid and other coagulants (picric acid, etc.) are not satisfactory since, as in the case of all other acid burns, they might seal acid products and thus delay healing.

STAGE 4

Immediately healing begins (7 to 10 days), the affected area may be dressed with a boric ointment which provides a satisfactory dressing until the scar produced is sound. Ultra-

^{11.} It is necessary to flush the affected parts thoroughly with warm water or warm alkaline solutions before the copper sulphate solution is applied, since, aside from the value of this form of treatment alone, the amount of phosphorus which can be inactivated by this method is small. The primary purpose of the copper sulphate is to destroy minute particles of phosphorus and to make obvious by blackening (formation of copper phosphide) the larger pieces so that they must be removed mechanically.

violet light radiation tends to reduce the great pain of skin lesions produced by phosphorus and also tends to promote rapid healing.

TREATMENT OF BURNS NEAR THE EYES

The simplest and safest procedure is to wash the parts well with warm water and apply a mask of lint soaked in sodium bicarbonate solution. The alkaline solution should be repeated every four hours. (The alkaline treatment must be thorough and the dressing must not be allowed to dry.)

TREATMENT OF INTERNAL INJURIES PRODUCED BY PHOSPHORUS-CONTAINING BULLETS

A careful search should be made for phosphorus diffusely implanted in tissues by looking for (a) fumes; (b) the characteristic odour of phosphorus, and (c) luminescence, and the affected parts should be washed thoroughly with warm water or, where permissible, warm solutions of sodium bicarbonate followed, if necessary, by warm water.

Where permissible, advantage should also be taken of very weak solutions of copper sulphate to inactivate the phosphorus. (Note: Copper sulphate is a poison. When taken in solution by mouth, it acts as an emetic. Most of it is thus lost by the energetic vomiting which ensues; but as little as 6 to 8 grains of absorbed copper sulphate have been reported as fatal.)

As the authors of the formula point out, owing to the high content of trichlorethylene, 12 the oil-soluble copper reagent precludes its use for internal injuries produced by phosphorus-containing bullets.

A Note on Acute Phosphorus Poisoning

Lethal dose.—White phosphorus is very poisonous when taken by mouth and, at one time, was a common form of poisoning, owing to its use in the manufacture of matches; this is now generally forbidden. As little as 2 mgm.

(the amount which was then generally used in the head of a match) is known to have caused the death of an infant; 3 mgm. caused the death of a child 2 years old, and the lethal dose in an adult is between 1 and 2 grains, though there have been cases of recovery following ingestion of 5 and 6 grains. Under air raid conditions, therefore, consideration will have to be given to the possibility of accidental poisoning of food from flying fragments of phosphorus bombs. The vapours of white phosphorus are also poisonous and, as stated, consideration must now be given to acute poisoning from phosphorus-containing bullets.

Signs and symptoms.—The signs and symptoms depend upon (a) whether the phosphorus has been taken by mouth or (b) whether it has entered the body elsewhere, as by means of a phosphorus-containing bullet.

In the case of ingested phosphorus, there are two phases, namely, (a) primary and (b) secondary. The signs and symptoms of the primary phase are due to local irritation of the stomach and intestines. The signs and symptoms of the secondary phase are due to the phosphorus which has been absorbed.

The early signs and symptoms may appear almost at once. The usual interval is 2 to 6 hours but, in rare cases, there may be a delay of 12 to 48 hours. They consist of a burning sensation in the throat, severe pain in the epigastrium, intense thirst, eructations of gas with a distinctive garlic-like odour, and vomiting, which may be very intense. The vomitus is dark green, black or coffee-coloured and may be luminous in the dark. The breath may also be luminous on account of small particles of phosphorus adhering to the mucous membrane of the mouth. Purgation may or may not occur. It is not common, but may be very severe and the fæces may also be luminous in the dark. The nervous and muscular debility is intense and death may occur from collapse or during a fit of convulsions within an hour. The fatal period may, however, be two and three weeks and more; but the average period is about five days.

Following the acute stage, which in most cases does not last longer than one to two days, there is usually an abatement of the signs and symptoms with a period of comparative comfort, except for general malaise. This period may vary from a few days to a few weeks. The secondary phase may, however, follow the first almost immediately. It is usually ushered in

^{12.} Trichlorethylene is a powerful narcotic. The fatal dose is about 2½ times only the dose necessary to produce acute narcosis. Like chloroform, it invariably causes death if the exposure to it is long enough and in high enough concentration. (Report No. 80. Toxicology of Industrial Organic Solvents. British Medical Research Council. Industrial Health Research Board.)

^{13.} Recipes for matches have been the subject of numerous patents. The phosphorus is, however, now of the red form. In safety matches, the phosphorus is on the rough side of the match-box, mixed with powdered glass, sand or emery and glue. The combustible is on the head of the match and generally consists of antimony sulphide mixed with potassium dichromate or some other solid oxidizing agent. When the match is struck, the friction changes a little of the red phosphorus to the white form which ignites readily.

by headache, great weakness, vomiting and diarrhea; but the striking features at this stage are (a) jaundice and (b) a marked tendency towards hæmorrhages in the skin and all mucous membranes, throat, bladder, uterus, vagina, etc. The abdomen becomes distended. The liver generally enlarges and becomes painful. The urine becomes scanty, is highly coloured and, in addition to bile pigments, albumin, blood and casts, may contain free fat globules. Though the pulse may be normal at first, it becomes progressively more rapid and weak as the prostration pro-The respirations become rapid and shallow and death usually occurs in about 5 days. In cases of longer duration, the liver may decrease in size towards the end, and death occurs from failure of liver function as in acute yellow atrophy. Though rare, cases have however been known to recover from this stage.

Post mortem appearances.—When death occurs within 24 hours, the findings are essentially those of a highly irritant poison with extensive destruction of the coats of the stomach by softening, ulceration and possibly perforation. On opening the stomach, white vapours may be noted. The garlic-like odour is generally marked and the stomach lining and contents exhibit luminescence. The mucous membrane may be inflamed or greyish-coloured due to cloudy swelling and fatty degeneration of the epithelium. If two days have elapsed since the ingestion of the phosphorus, the degeneration of the large glandular organs and heart muscle is generally well developed. If three or more days have elapsed, the picture is usually characteristic. The skin is yellow and contains petechiæ. Petechiæ may also be present in the pleura, pericardium and mesentery. female, hæmatomata may be found in the ovaries and uterus. The soft organs show icteric discoloration and a high degree of fatty degeneration, as do also the muscles, including the heart muscle. The liver is practically always enlarged, has a saffron-yellow colour with red spots, and has a pulpy consistency. On section, the surface is very greasy, and though the colour is usually of a uniform yellow tint, it may be "marbled" from the presence of unaltered liver tissue. On microscopic examination, there is the typical picture of fatty degeneration. The fat globules found in the Kupffer cells appear to be an early manifestation. Degenerative changes and hæmorrhagic areas may be found in the brain and spinal cord. When death occurs after

a prolonged secondary phase, the stomach may actually appear normal. Putrefaction supervenes rapidly after death.

TREATMENT

Under no circumstances should oily or fatty materials, such as milk, be administered to alleviate the gastric irritation, as these aid absorption of phosphorus.

Copper sulphate should not be used as an emetic, though some of it might convert the phosphorus into non-igniting copper phosphide. Aside from possibly adding to the irritation of the stomach, there is a danger of some of the copper sulphate being absorbed owing to destruction of the gastric mucosa.

Prompt lavage of the stomach with warm potassium permanganate solution (about 3 grains to the pint) is the safest inactivating agent.14 It oxidizes the phosphorus, and the phosphorus acids produced are rendered harmless by dilution. The irrigation should be continued until the colour of the returned liquid remains unchanged. Quarts of the solution may be required, if the stomach contains food. After the irrigation, the stomach should be washed well with warm water and Epsom salts should be left in the stomach to promote catharsis.15 The dose should be repeated as often as required, to encourage elimination, for several days. If diarrhea has occurred, the bowels should be flushed with the warm dilute potassium permanganate solution.

Diuresis should be encouraged by repeated intravenous injection of a 5% solution of glucose. This will also tend to decrease the danger of hypoglycæmia, and tend towards storage of glycogen in the liver and thus tend to reduce the degree of fatty degeneration. If necessary, morphine should be given to relieve the pain. Sodium bicarbonate should be administered to combat the acidosis, which may be severe owing to the phosphorous acids formed. A level teaspoonful (about 5 grams) in a half glassful of water should be given every half hour until the urine becomes alkaline or until the person has received about 0.5 grams per kilogram of body weight. If the alkali is not tolerated by mouth, a litre of a 3% solution may be given intravenously. Further treatment is symptomatic.

15. Phosphorus may be found in the fæces as long as a week or more.

^{14.} Care must be taken to dissolve the crystals of potassium permanganate completely. Solid potassium permanganate is a corrosive.